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# **REPORT ON SPQ-94-4098**

"HETEROSTRUCTURES (CaSrBa)F2 ON InP FOR OPTOELECTRONICS"

by

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#### **Abstract**

Temperature-reduced MBE growth of group II-a fluorides onto InP(100) surface as well as optimal cleaning and passivation procedures for InP wafers have been newly developed taking into account exsisting literature data. High quality BaF<sub>2</sub> and SrF<sub>2</sub> layers onto InP(100) have been grown at 350°C under ultra-high vacuum conditions using epitaxial and bulk substrates. MBE and Laser Vacuum Epitaxy (LVE) growth methods for semiconductor-semiconductor (SS) and semiconductor-crystalline dielectric-semiconductor heterostructures are considered as well as experimental facilities for these processes are elaborated.

**Keywords:** group II-a fluorides, passivation, cleaning, Molecular Beam Epitaxy (MBE), Laser Vacuum Epitaxy (LVE), semiconductor-semiconductor (SS), semiconductor-crystalline dielectric (SCD ), BaF<sub>2</sub>/InP(100) and SrF<sub>2</sub>/InP(100) heterostructures.

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#### **Preface**

The presented report deals with growth methods of IIa group fliorides {(CaSrBa)F<sub>2</sub>} thin films on InP(100) substrates, including methods of cleaning and passivation of substrates, as well as ex situ and in situ characterization of substrate surface, interface and fluoride overlayer. Growth of the isolating fluoride layer onto a semiconductor substrate in optoelectronic integated circuitries (OEIC) structure fabrication for some important cases is only an inmediate stage for the next cristalline overlayer growth, so some methods of cristalline semiconductor thin film growth are also reported, mainly, those of them which were realized by the author and his collegues from Laser Research Laboratory (LRL) or in collaboration with outer organizations and could be useful for nondestructive temperature reduced heteroepitaxy onto pre-made device structures.

In principle, IIa group fluoride film growth on semiconductor substrate and even the next crystalline semiconductor overgrowth for a few scientific and industrial centers are routine operations, but not all of those centers willingly publish their high technogical know-how's in this promissing sphere of opto- and microelectronics. Besides, concrete technological contrivances are dispersed in a lot of papers as well as open publications on closed technological cycles of semiconductor-crystalline dielectric-semiconductor (SCDS) for OEIC's are very scant. At the present report to the U.S. Air Force European Office of Aerospace Research and Development (EOARD) the author tried to avoid the noted above shortcomings, taking into account the bilateral intention to develop collaboration between EOARD and LRL as well as that the author's personal experience and possibities of his lab could be useful in SCP growth and OEIC fabrication. Therefore, at the report a considerable attention is given to the description of our achievements in preparation and study of some advanced semiconductor materials and structures of the type of semiconductor-semiconductor (SS).

# 1. SHORT REVIEW: Main results on growth of group II-a fluorides on semiconductors

InP is an important semiconductor material because of its high carrier mobility and hence its potential application for various microelectronic devices, such as high frequency metal-dielectric-semiconductor field effect transistors (MISFETs), solar cells, photoelectrical cells, Schottky diodes, and optoelectronic integrated circuits (OEIC)[1,2,3]. This technological aspect explains the current interest in understanding of basic properties of InP surfaces and their passivation overlayers. Although the (001) surface only is technologically important, basic physical properties were investigated mainly on the InP(110) surface, because this is the cleavage plane which can easily be prepared in ultrahigh vacuum (UHV).

High quality InP(110) cleavage planes with low defect concentrations show flatbands independent of the bulk doping. Therefore at these surfaces the position of the Fermi level  $E_f$  can be shifted through the band gap by different doping concentrations. The position of  $E_f$  is however pinned on (110) surfaces with high defect densities [4]. In earlier studies on InP(001) surfaces low-energy electron diffraction (LEED) structures were observed which were interpreted as  $(4x1)45^{\circ}$  and  $(8x2)45^{\circ}$  reconstructions [5,6]. Now there is general agreement that InP(001) forms a (4x2) reconstruction after a sputter and anneling preparation procedure [7]. There is no experimental study or proof of Fermi level pinning at InP(001). The oxidation of this surface with the aim of obtaining good quality passivation layers was investigated extensively by several groups [see, for instance, 8]. Different oxidation methods were used, but always nonstoichiometric mixed oxides were formed, leading to high concentrations of electronic trap states in the band gap. In this context ordered layers of  $Al_2O_3$  on InP(001) were also prepared [9], but due to the high lattice mismatch of 10% these layers form cracks for thicknesses above 3 nm.

Recently, group-IIa cubic fluorides, CaF<sub>2</sub>, SrF<sub>2</sub> and BaF<sub>2</sub>, have received considerable attention as epitaxial dielectric films on semiconductor substrates because they have a cubic crystal structure similar to the diamond structure of Si and the zinc-blende structure of the III-V compound semiconductors.[10-33]. Their large electronic bandgaps make them interesting for the development of new metal-insulator (MIS), and metal-insulator-semiconductor fieldeffect transistor (MISFET) structures and for achieving the long-range goal of building threedimensional devices. In addition, CaF2, SrF2 and BaF2 molecules can be sublimed from a Knudsen-cell type oven congruently due to their high energy of dissociation, automatically solving the problem of film stoichiometry. CaF<sub>2</sub> forms high quality epitaxial films on Si surfaces [10] and therefore the earth-alkali-fluorides are promosing candidates for passivation layers also on InP(001) surfaces. Because the lattice parameters of the fluorides bracket those of semiconductors such as Si and InP, it is possible to grow a mixture of the fluorides which is lattice matched to the substrates [10]. If such single-crystalline lattice-matched dielectric films can be grown on a semiconductor substrate, the interface trap densities, in principle, can be reduced and the electrical properties of the insulator-semiconductor interface improved [18]. The possibility is specially interesting for III-V compound semiconductors because of the lack of good insulating films on the III-V materials. Indeed their crystalline cubic fluoride structure is very similar to the III-V semiconductor zinc-blende structure. Thus, it may be possible to grow a heteroepitaxial dielectric semiconductor structure and consequently to reduce the density of electronic localized states at the interface. Indeed, parameters (5. 4460 A, 5.7996 A and 6.2001 A, at room temperature, for CaF<sub>2</sub>, SrF<sub>2</sub> and BaF<sub>2</sub> respectively) are very close to those of both GaAs (5.6534 A) and InP (5.8694 A). Moreover, some mixed group II-a cubic fluoride alloys can be exactly matched to GaAs and InP. Indium phosphide semiconductor was one of the substrates used by Farrow et al. [10] in their pioneering work on epitaxial growth of group II-a fluorides on semiconductor surfaces. They successfully grew single crystal BaF<sub>2</sub> films on this substrate by molecular beam epitaxy (MBE).

Since epitaxial growth of  $CaF_2$  onto Si was reported in 1981 for the first time[10], much work was done to characterize the geometric and electronic structure of epitaxial group II-a fluoride layers and of the semiconductor-insulator interfaces. This was done on different orientation of Si [16, 17, 25, 35, 36], GaAs [27, 28, 30] and on InP substrates [14, 25-27, 30-33]. Very interesting compound of group II-5 fluorides is  $CdF_2$  which was recently grown on Si(111) by MBE method [37,38]. It has the same fluorite structure as group II-a fluorides. However, their electronic properties are different. Undoped  $CdF_2$  crystals are good insulators (the band gap is equal to 8 eV). Being doped with trivalent impurities and annealed they convert into a semiconductor state with binding energy of shallow donor levels about 0.1 eV and free electron concentration up to  $4x10^{18}$  cm<sup>-3</sup> [39]. Another remarkable property of  $CdF_2$  is the efficient multicoloured electroluminescence which is observed in the crystals doped with Mn or rare earth impurities [40]. It is favorable for growth of pseudomorphic layers and coherent  $CdF_2$  -  $CaF_2$  superlattices on Si substrates (the lattice mismatch between  $CdF_2$  and Si is only - 0.8%).

In 1982, Sullivan et al.[14] showed the possibility of obtaining  $BaF_2$  /InP(100) and  $CaF_2$ /InP(100) epitaxial structures by MBE method. Phillips et al. [15] also reported the growth of  $BaF_2$  films of high crystalline quality on InP(100) and of somewhat inferior quality on InP(111) surfaces. However, in these cases, the lattice parameter of the insulator (6.2009 A and 5.4629 A, respectively) is slightly different than that of the semiconductor (5.8694 A). Tu et al. [16, 17, 25] reported the successful epitaxial growth of  $BaF_2$ ,  $SrF_2$  and  $CaF_2$  on InP(100) and, subsequently, the growth of double heterostructures [16] consisting of epitaxial InP/ $CaF_2$ /InP(001) by MBE. The authors of the papers [16, 17, 25]made also the first attempt to grow an epitaxial lattice-matched mixed fluoride ( $Ba_xCa_{1-x}F_2$ ) film on InP(001) by MBE. Although  $BaF_2$  and  $CaF_2$  form a solid solution only when the concentration of one of the

constituents is less than a few percent [25, 33], these workers were able to obtain a mixed fluoride which had a lattice constant consistent with x = 0.2. Nevertheless, they did not grow films which were exactly lattice matched (x = 0.56) to InP, even though they believed the fluxes from the  $BaF_2$  and  $CaF_2$  ovens to be consistent with the formation of such a lattice-matched fluoride.

Better results were obtained with alloys of  $BaF_2$  and  $SrF_2$  (a = 5.7996 A) by Tu et al. [16]. These authors have grown the solid solution  $Ba_{0.44}Sr_{0.56}F_2$  and  $Ba_{0.2}Sr_{0.8}F_2$  [16, 17] on InP(100) by molecular-beam epitaxy (MBE). Sinharoy et al. [26] reported the successful epitaxial growth of strontium fluoride on InP(100) in a conventional UHV system that was not equipped with a phosphorus or iodine vapour source.  $SrF_2$  was chosen for these experiments because among the group II-a fluorides it has the lowest lattice mismatch (-1.2%) with InP.

Many results dealing with the structural properties of these group II-a fluorides / InP systems have been published, utilizing various techniques including Rutherford backscattering (RBS), reflection high-energy electron diffraction (RHEED) and transmission-electron microscopy (TEM) to evaluate the quality of the epitaxial layers. However few results concerning their electrical properties are available.

Bulk studies have shown that BaF<sub>2</sub> and SrF<sub>2</sub> do form a solid solution at all compositions and that Vegard's law is obeyed [34]. To precise match the lattice parameter of Ba<sub>1-x</sub>Sr<sub>x</sub>F<sub>2</sub> with InP, Vegard's law predicts that the molar fraction x would be equal to 0.825 at room temperature. Thus in a first attempt, Couturier et al. [27] tried to prepare Ba<sub>0.175</sub>Sr<sub>0.825</sub>F<sub>2</sub> thin films by sublimation under vacuum of a solid solution powder. Unfortunately, Rutherford backscattering and infrared-absorption studies revealed a change of Ba/Sr ratio along the depth of the grown layers [28], which shows that this compound does not undergo congruent sublimation. Thus a composition defect has been noted along the depth of the layers. Barriere et al. [30] suppose that this could explain the extrinsic ionic conductivity of the films and the important hysteresis phenomenon observed in the C-V data of metal-(BaSr)F<sub>2</sub>-InP structures.

Weiss et al. [31] reported on the epitaxial growth of CaF<sub>2</sub> and SrF<sub>2</sub> onto the technologically important InP(100) surface. The authers of the paper [31] characterized the morphologies of the epitaxial fluoride layer surfaces with low energy electron diffraction (LEED) and atomic force microscopy (AFM) and determined the growth orientation of the layers with LEED. They have shown that both fluorides grow in (001) orientation in their cubic bulk structure onto the (001) substrate and form atomically rough surfaces consisting mainly of (1x1) ordered (111) facets.

As a consequence it has been preferred by the authers of the paper [27] to symply study (mainly, structural and electrical properties) of SrF<sub>2</sub>/InP(100), the lattice parameter mismatch between these two compounds being only 1.17% [26]. Couturier et al. [27] have shown that in the case of metal-insulator-semiconductor (MIS) SrF<sub>2</sub>/InP diodes prepared by sublimation of the fluoride under vacuum, an important modulation without hysteresis of the surface potential of the semiconductor can be noted for sweep frequencies down to 1 Hz. In this case the surface density state N<sub>SS</sub> in the depletion region of the semiconductor is about 10<sup>11</sup> eV <sup>1</sup>cm<sup>-2</sup>. Barriere et al.[30] using Rutherford backscattering, X-ray diffraction and X-ray photoelectron spectroscopy (XPS) studied in details the composition of such SrF<sub>2</sub> thin films and the interaction between this fluoride and InP(100) substrate. Note that the authors of the paper [30] grew the thin films of SrF<sub>2</sub> by sublimation under a classical vacuum (10<sup>-7</sup> Torr). They showed by Rutherford backscattering and by XPS measurements that the obtained layers were quasistoichiometric and fluorine is chemically bound with indium and phosphorus at the interface. These phenomena could explain a hysteresis occured on the C(V) characteristics of metal-insulator-semiconductor (MIS) diodes for low-sweep frequences due to an ionic migration along the grain joints as well as a relatively low density of surface states N<sub>ssn</sub> at the depletion region of semiconductor measured by Couturier et al. [27]. Except the ionic transport such quasistoichiometric texturized structure can favor also water absorption following by chemical reactions with the fluoride. For the noted above reasons Barrier et al. [32] have changed the preparation conditions and obtained the  $SrF_2/InP(100)$  structures under ultra-high vacuum. It was shown [32] that at some experimental conditions the obtained films are stoichiometric, homogenious, and quasi-insensitive to air exposure.

Metal-insulator-semiconductor (MIS) structures and semiconductor-crystalline dielectric-semiconductor (SCDS) structures have been prepared by growing epitaxial CaF<sub>2</sub> layers on InP(001) substrates as determined by RHEED. In addition, their electrical properties were characterized by C-V measurements [16, 27,]. Weiss et al. [29]reported detailed information from ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS) about electronic interface properties of this overlayer system. In the paper [29] the authors reported also on the reproducible preparation of two different InP(001) surface reconstruction, a (4x2) structure with streaks at the half order spot positions that were identified as a disordered c(8x2) structure which was obtained after high temperature annealing leading to excess metallic In<sup>0</sup> on the surface. They also investigated by LEED, XPS and UPS the epitaxial growth of CaF<sub>2</sub> from the submonolayer range up to layers of 10 nm thickness and have got the growth orientation, the local structure of thick overlayers and the eletronic scheme of the interface as well as discussed the nature of defects near interface. The authors also have determined the valence band and compared it with predictions from the electron affinity rule.

Lattice-matched single-crystalline insulators are also important for epitaxial semiconductor-crystalline dielectric-semiconductor structures (SCDS) in allowing the growth of a better quality top epitaxial semiconductor layer. Ishiwara and Asano have grown Ge/Ca<sub>x</sub>Sr<sub>1-x</sub>F<sub>2</sub>/Si(111) by vacuum evaporation [11], where Ca<sub>x</sub>Sr<sub>1-x</sub>F<sub>2</sub> is lattice matched to Ge. Tu et al. have grown by molecular-beam epitaxy (MBE) the first epitaxial III-V SCDS double heterostructures with InP/fluoride/InP(100), which may be potential for novel devices in three-dimensional integrated circuits (3-d IC's) and in monolitic integrated optics [16]. The surface morphology of the insulating overlayers is important, e.g., for the preparation of (SCDS) structures by growing a second semiconductor onto the insulator overlayer.

# 2. GROWTH METHODS OF SEMICONDUCTOR-SEMICONDUCTOR AND SEMICONDUCTOR-CRYSTALLINE DIELECTRIC-HETEROSTRUCTURES

#### 2.1. Introduction

Different components of OEIC serve very diverse operations including receiving, transformation, processing and transmission both of optical and electrical signals spreading in extremally wide frequency region. It is obvious so, that such characteristics for OEIC device as, for instance, a photocell matrix receiver or light emission diode array, could be performed only on the base of heterostructures, consisting of the materials which have strongly different characteristics such as their electric and optical properties as well as their crystal structure and lattice parameter, thermal and mechanical properties or degradational parameters. Therefore, formation of perfect interface between various heterpairs is a rather complicated problem. Indeed, differencies in crystal structure and lattice parameters, thermal expansion coefficients, hardness and plasticity, stability to environment make a lot of obstacles for perfect interface formation, single crystal overlayer growth as well as for fabrication of the OEIC chips with good degradational parameters. Especially complicated this problem is in the case of high quality p-n or p-i-n heterjunction regions incorporated into an OEIC chip. In

principle, the problem is solved by various temperature reduced heteroepitaxial methods, some of them are discussed below.

# 2.2. Heterostructures of the type of semiconductor-semiconductor (SS)

Growth of the type SS heterostructures for p-n junctions can be fulfilled by liquid phase epitaxy (LPE), gas transport epitaxy (GTE), molecular organic vapour phase epitaxy (MOVPE), molecular beam epitaxy (MBE) as well as by some other methods.

Essential achievements have got in that case when crystal structures, lattice parameters as well as temperature expansion coefficients of the chosen heteropair materials have not considerable differences (it is known, for instance, that for growth of heterostructure by the above noted classic methods the lattice period mismatch must not exceed appr. 1%). Therefore, out from the possible conjugation are a lot of the advanced heteropairs such as Si/GaAs (4.05%), Si/InP (7.92%), Si/InAs(11.6%), Si/InSb (19.3%) and others, as well as the combinations of III-V materials such as GaAs/InP (3.72%), GaAs/InAs (7.26%), GaAs/InSb (14.7%) and others (the mismatch is counted relatively to the Si or GaAs substrate respectively; see the Table I: Lattice parameters, band gaps and current carrier mobilities for some semiconductors).

Table I. Lattice parameters, band gaps and current carrier mobilities for some semiconductors

| Semiconductor | Lattice constant a <sub>o</sub> (A) | Energy gap<br>E <sub>g</sub> (eV) | Mobility (300 (cm <sup>2</sup> /V sec) |       |
|---------------|-------------------------------------|-----------------------------------|--|-------|
|               | <u>u<sub>0</sub> (11)</u>           | Lg (0 1 )                         | Electrons                              | Holes |
| Si            | 5.4310                              | 1.11                              | 1400                                   | 470   |
| Ge            | 5.6461                              | 0.67                              | 3900                                   | 1900  |
| GaP           | 5.4506                              | 2.26                              | 110                                    | 75    |
| GaAs          | 5.6535                              | 1.42                              | 8500                                   | 400   |
| AlAs          | 5.6605                              | 2.17                              | 280                                    |       |
| InP           | 5.8688                              | 1.35                              | 5000                                   | 150   |
| InAs          | 6.0584                              | 0.36                              | 33000                                  | 460   |
| GaSb          | 6.0954                              | 0.72                              | 5000                                   | 850   |
| AlSb          | 6.1355                              | 1.58                              | 900                                    | 450   |
| InSb          | 6.4788                              | 0.17                              | 80000                                  | 1250  |
| ZnSe          | 5.6676                              | 2.80                              | 530                                    |       |
| ZnTe          | 6.0880                              | 2.20                              | 530                                    | 130   |
| CdTe          | 6.4816                              | 1.49                              | 700                                    | 60    |

Some possibilities for a good conjugation of the materials having of (1-3)% of mismatch at p-n junction preparation gives an oblique cutting of a substrate forward to its main (100) or (111) planes [see, for instance, [41] which lets to a small increase in one direction the lattice parameter (up to 3-4%), but this operation makes the substrates too expensive and unconvinient for application, besides, due to the differences in the temperature expansion coefficients time degradation of some heterostructures can be essential.

To form an interface between two semiconductors with different lattice parameters and/or crystal structures methods of active modification of the substrate surface are widely used. These methods are aimed to conjugate smoothly the mechanical and thermal properties of the materials as well as to overcome the creation of numerous misfit dislocations. Among these methods may be mentioned superlattice or buffer layer formation, the application of a low energy ion source of Group V elements in III-V compound growth [42] and so on. But these methods of conjugation, as a rule, could not be accepted for a good interface formation because they do not supply necessary electric properties of a p-n heterojunction.

That to form perfect interface between heteropairs having a strong differences in the type of crystal structure, lattice periods as well as thermal expansion coefficients, at our laboratory since 70-th is developed the method of laser vacuum epitaxy (LVE) which gives an opportunity to smoothly conjugate various materials (see, for instance [43-48]).LVE is a very interesting method for this purpose because atoms and ions in a laser produced plasma effectively re-evaporate matter of the substrate and penetrate into it due to their relatively high density and kinetic energy. In [48] LVE was used as the first stage of film growth in order to modify the substrate surface and to obtain a smooth conjugation of lattice parameters, as well as thermal and mechanic characteristics of both III-V film and Si substrate; the second stage of film growth up to thicknesses which are typical for microelectronic applications (1-2  $\mu$ ) was fulfilled with the help of GTE or MOVPE. We have shown the importance of LVE for the formation of perfect interfaces between the materials with considerable mismatch of lattice periods, thermal and mechanical characteristics such as Si/GaAs, Si/InP and Si/InAs. Besides, we tried to choose the composition of LVE produced intermediate layers which would give the best results at minimum thickness of the layer as well as to check the compatibility of LVE with other growth methods, especially with GTE and MOVPE.

The experimental set-up for LVE is shown in Fig. 1. In the chamber (1) with residual atmosphere of  $10^{-8}$  Pa one can see the pulse laser (2) which evaporated the target (3) (2 mm thick GaAs, InP or InAs plates), the substrate (4) heated by a thermal (5) or by a laser (2) heaters ( the latter heats the substrate just a few microseconds before a new portion of the condensate (6) from the laser produced plasma (7) of the target material enters the substrate). Depending on the type of the laser (2) its characteristics are: the pulse energy 0.1 - 1.0 J; the pulse duration  $10^{-8} - 10^{-11}$  s; the repetition frequency 10 - 100 Hz and the wavelength 0.337 - 1.06 µm.

The plasma cluster (7) and the condensate (6) differ in composition: the first consists of only atoms and ions of the target material in a ratio of appr. 9:1 at the laser power density of 10 8 W/cm² while the latter contains both the target material particles and re-evaporated substrate material particles which are thermolized in the counter flow. The ratio between the target and the substrate particles depends on the laser power density. This ratio changes from pulse to pulse in the direction of the target material (see Fig.2). Monitoring of the composition, density and energy of the condensate (6) and the cluster (7) was made with the help of an optical system (8), a monochromator (9), PMT (10), boxcar-integrator (11), computer (12) and display system (13). The standard set of diagnostic equipment inside the chamber (1) includes an Auger spectrometer (14) with an argon gun (15), a mass-spectrometer (16) and low (LEED) and fast (RHEED) electron diffractometers (17). With the help of the effusion cells (18) it was possible to change the ratio of the group III and group V

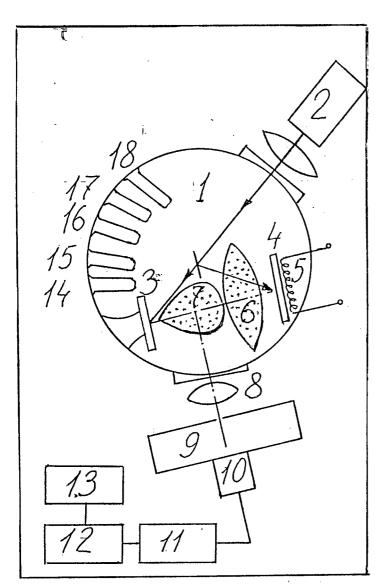


Fig.1. LVE experimental set-up.
1.Growth chamber. 2.Pulse laser. 3.Evaporated target.
4.Substrate. 5.Thermal heater. 6.Thermolized condensate consisting of target and substrate particles.
7.Laser produced plasma. 8.Condensor.
9.Monochromator. 10.Photomultiply tube.
11.Boxcar-integrator. 12.Computer. 13.Display.
14.Auger spectrometer. 15.Argon gun.
16.Mass-spectrometer. 17.LEED and RHEED.
18.Knudsen cell.

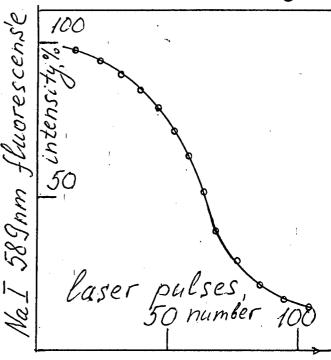


Fig.2. 589.0 nm Na(I) spectral line intensity vs number of laser pulses evaporating GaAs target. LVE growth of GaAs on NaCl substrate

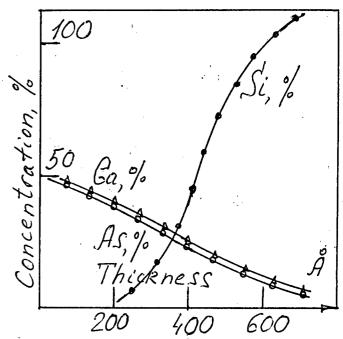


Fig.3. Distribution of Ga, As and Si concentration inside LVE produced intermediate layer according to Auger spectroscopy measurements.

elements in the condensate (6) or to prepare by MBE fluoride or semiconductor overlayer. Thus, the described apparatus developed at our laboratory can be used not only for SS structure preparation but also for growth of SCDS structures in a commom cycle, consisting of LVE and MBE methods.

GTE and MOVPE were also used for the growth of InP (GTE in collaboration with Dr.hab. Emil Russu from the Semiconductor Materials Center of the Institute of Appl. Physics Mold. Ac.Scie., Kishinev, Moldova) or GaAs (MOVPE in collaboration with Dr. Carlo Flores and his colleagues from CISE-s.p.a., Segrate, Milan, Italy) layers on the substrates or intermediate layers grown by LVE. The thickness of the layers grown by these one or two step methods was 1-2 µm and the growth temperatures were 450 and 650°C for GTE and 450 and 700°C for MOVPE. Due to the fact that these growth temperatures were considerably more than it is necessary for non-destructive temperature reduced epitaxy of SS and SCDS structures in future we will use mainly LVE and MBE in a common cycle with the help of the apparatus presented in Fig.1.

The ion component of the target flow caused sputtering of the substrate and of the growing film [43,48]. This sputtering effect in LVE method was directly observed during condensation of a semicunductor target material onto a substrate. For instance, Fig.2 demonstrates this phenomenon for GaAs condensation onto NaCl substrate. NaCl substrate is more convenient for this kind of experiment due to intense fluorescence of Na atoms at 589.0 nm. Fig.2 shows the dependence of fluorescence intensity of the 589.0 nm spectral line registered a few mm apart from NaCl substrate on the number of laser pulses evaporating GaAs target. The decrease in fluoresence intensity shows that each portion of the material reevaporated from the substrate surface contains a lower quantity of the original substrate material than the previous one. It has been also shown with the help of the secongary ion mass-spectroscopy (SIMS) and Auger spectroscopy of layer by layer etched surfaces that in an LVE grown heterostructure there is a clearly determined buffer layer, the composition of wich smoothly changes from the substrate to the target material (see, for instance, Fig.3 for the case of LVE grown GaAs on Si. Depending on the growth conditions the thickness of the intermediate layer between substrate and eveporated material changes within the 0.02-0.1 µm. It was shown [43,48] that the intermediate layer is a metastable solid solution having the composition of the type of  $T_{1-x}$  -  $S_x$  (GaAs<sub>1-x</sub> - Si<sub>2x</sub> in the case presented in Fig.3). This intermediate layer (primer) obtained by LVE method has been used for the next growth of a semiconductor overlayer at the initial stage of our investigations by GTE and MOVPE methods [48]. All the results give clear indications of the important role of laser deposited intermediate layers in the formation of interfaces between semiconductors having big lattice mismatch and considerable differences in thermal and mechanical characteristics of the chosen heteropairs. Therefore, the LVE method developed at our laboratory seems to be very perspective for p-n heterojunction growth. Besides, the method is compatible with MBE due to similar (practically, the same - see Fig.1) technological and diagnostical equipment that give an opprtunity to organize a common cycle of SS and SCDS structure growth inside the same apparatus.

# 2.3. Heterostructures of the type of semiconductor-crystalline dielectric (SCD)

# 2.3.1. Introduction

In device structure of the traditional 2d-electronics a grown epitaxial semiconductor layer is covered by unoriented (polycrystalline) metal or dielectric layer. The next epitaxial growth onto unoriented surface is impossible except some special procedures such as transplantation of a ready-made epitaxial structure [49] or shock crystallization from overcooled liquid, which can be realized, in particular, by the LVE method [43].

It is obvious that growth of an epitaxial semiconductor-crystalline dielectric-semiconductor (SCDS) structure is possible only if insulating layer grown as a single crystal has crystal structure and lattice parameter similar to semiconductor layers disposed under and over it. It was shown in the Part I of the report that the group II-a fluorides are good materials for heteroepitaxial growth onto Si and III-V semiconductor surfaces (see Table 3); it is possible also to match through the fluoride layer Si with all the III-V compounds as well as to grow hetero- and homostructures of the type of III-V/III-V. Therefore, growth of SCDS structures using the group IIa fluorides is a key point for the development of 3d-electronics and various OEIC structures.

Growth of an epitaxial fluoride layer onto a single crystal semiconductor substrate is the first stage of SCDS structure preparation. This stage is important also in MIS structure preparation due to the fact that some semiconductors have not own perfect oxide as well as that crystalline insulators have good dielectric properties and misfit dislocation density at the semiconductor-dielectric interface some order less compared to unoriented dielectric layer. Some experience of the Laser Reserch Laboratory in MBE growth of some group II-a fluorides on Si (see, for instance [50-52]) also shows that this process can be easily combined in common cycle with LVE for preparation of various SCDS heterostructures.

# 2.3.2. InP(100) substrate characterization, passivation and cleaning

#### 2.3.2.1. Substrate characterization

Three group of InP(100) substrates were used for passivation, cleaning and epitaxial growth experiments.

That to elaborate passivation and cleaning procedures InP(100) wafers produced by Chohralsky method at the Institute of Applied Physics of the Academy of Sciences of Moldova (IAP ASM) were used. They have 40 mm diameter, 350µ thickness, n-type and appr. 10<sup>18</sup>cm<sup>-3</sup> concentration, appr. 10<sup>5</sup> cm<sup>-2</sup> density of dislocations (etched pitch density - E.P.D.) and mirror polished (100) or 1° of toward [100] sides. After their growth, cutting and polishing the samples were keeped in non-hermetic containers at atmospheric air.

For elaboration of the growth procedures for  $BaF_2$  and  $SrF_2$  onto InP(100) we used samples produced by: 1)IAP ASM , 2) Rome Laboratory at Hanscom AFB, MA and 3) Japan Energy Corporation(JEC, formely Nippon Mining and Nikko Kyodo Co LTD, Tokyo, Japan). Samples (1) with the noted above parameters were exact oriented or  $1^0$  off toward [100] InP(100) mirror polished wafers, sample (2) was appr.  $0.5\mu$  of the thickness and have  $1.5cm^2$  n-type epitaxial layer grown on Fe-doped semi-insulating exactly oriented InP(100) substrate and sample (3) used for final epitaxial growth of  $SrF_2$  was exactly (100) oriented wafer, produced, treated and induvidually packed by JEC with the parameters, presented in Sertificate (see Fig.4).

Note, that for each of the three group of samples depending on their pre-history different procedures of surface treatment before epitaxial growth are necessary. For samples (1) deep cleaning and/or surface passivation are very effective, epitaxial layer(2) needs only a weak heating inside the UHV growth chamber and for samples (3) no (or very weak) pre-treatment is necessary.

#### 2.3.2.2. Passivation of InP(100) surface

Passivation procedure is applied for deoxidation, stabilization and improvement of InP surface with the help of S atoms bonding In and P dangling bonds. The passivation leads to reduction in the surface recombination velosity due the reduction of the surface defect density. The reduction of the surface defect density is obeyed to etching effect of  $(NH_4)_2S_x$  (ammonium sulphide) solution used for the passivation [53,54]. It was shown [54] that InP(100) is etched at the rate of 20 -30 A/h when the sample is treated with the solution at

# **ACROTEC**

Customer: Head of the Laser Research Lab

# CERTIFICATE

Product : InP Wafer

Ť

Spec No.

: -

Lot Nó.

:1S5321PSN

Wafer No.

:No.27

Quantity

:1.

JAPAN ENERGY CORPORATION .

Package Number

:1

Isohara Plant

Inspection Date

:Mar.20,1995

187-4 Usuba, Hanakawacho, Kita-ibaraki,

Certificate No.

:503S02PSN

Ibaraki 319-15, Japan

| T.                |                                       |                          | T                 |
|-------------------|---------------------------------------|--------------------------|-------------------|
| Item              | Specifications                        | Measurements             | Unit              |
| Growth Method     | LEC                                   | LEC                      | •                 |
| Conductivity Type | n ·                                   | n                        |                   |
| Dopant            | Sn                                    | Sn                       |                   |
| Carrier Density   | $(0.5 \sim 6) \times 10^{18}$         | 1.3 × 10 <sup>18</sup>   | cm - s            |
| Mobility          | <del></del> ·                         | -                        | cm²v-¹sec-¹       |
| Resistivity       | _                                     |                          | Ωcm               |
| E. P. D.          | ≦ 3 × 10 <sup>4</sup>                 | < 1 × 10 <sup>4</sup>    | cm <sup>- 2</sup> |
| Orientation       |                                       | -                        | degree            |
| Thickness         | approx.350                            | 346                      | μm                |
| T. V              |                                       | _                        | μπ                |
| Bow               |                                       |                          | μm                |
| Finish (Surface)  | Mirror Polished(Etched)               | Mirror Polished(Etched)  |                   |
| (Back)            | Etched                                | Etched                   |                   |
|                   | Individual N <sub>2</sub> gas package | Individual N₂gas package | 4.                |
| Size (Diameter)   | 50 ± 1                                | 50.3                     | mm                |
| Orientation Flat  |                                       |                          |                   |
| a) Orientation    | -                                     | _                        | degree            |
| b) Width          | _                                     | _                        | mm ,              |
| Index Flat        |                                       |                          |                   |
| a) Orientation    | -                                     |                          | degree            |
| b) Width          | _                                     | _                        | mm                |

Fig. 4. JEC's InP wafer certificate

, J. Anan

Manager of Quality Assurance Section

45°C. These features are needed to fabricate surface devices and to garantee realibility as well as to prevent the adsorption of oxygen.

The method of passivation according to our AES analysis decreases content of oxigen to less than 0.1%ML and RHEED gives (2x1) reconstruction after heating inside UHV chamber at appr. 300°C during 10 min, but, unfortunately, carbon contamination was still rather high: 0.5-1.0%ML. Note, that in the case of Si well-cleaned surface we had C concentration also less than 0.1%ML because another chemical treatment procedure without passivation has been used. Probably, passivation does not effect on C contamination - see, for instance, Fig. 5 reproduced from [54]. Compared to the AES spectra from [54], our spectra are the same, but carbon peak is more intense.

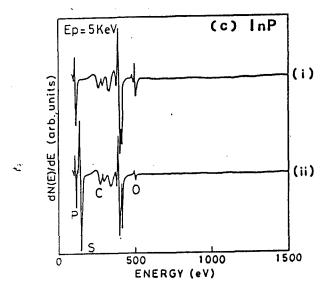


Fig. 5. AES spectra on InP(100) surface before (i) and after (ii) the (NH<sub>2</sub>)S<sub>x</sub> treatment

Let us shortly consider the proposed model for the passivation of InP surface with  $(NH_4)_2S_x$  treatment and the passivation procedure [53]. The natural oxide and presumably defective portion of InP is etched away in that ammoniun sulfide solution and the fresh surface of InP is terminated with a monoatomic layer of sulfur. The sulfur-terminated surface has no dangling bonds, that is, the surface does not accept chemically adsorbing atoms. The energy released by physically adsobing atoms is insufficient to create In and P vacancies, which cause interface trapping centers. Thus, the surface of InP is very effectively passivated and stabilized by this treatment.

The as-etched wafers were freshly prepared by etching with a  $H_2SO_4$ - $H_2O_2$ - $H_2O$  (1:1:4) solution and then thoroughly rinsed in deionized (DI) water. The etched samples were dipped into a solution of  $(NH_4)_2S_x$  (pH ~ 8) with 8% of excess sulfur, blown dry with  $N_2$  gas and then transferred into UHV chamber. A thin film of residial deposit of amorphous sulfur is usually observed on the surface but it is easialy removed keeping the surface in a vacuum at room temperature.

The effect of  $(NH_4)_2S_x$  treatment on InP properties is observed as follows (Oigawa et al. [54]): 1) enhancement in PL intensity; 2) removal of oxigen atoms on the surface; 3) clear dependence of the Schottky barrier height on the work function of the contact metal as well as 4) improvements in C-V characteristics of MIS structures.

According to [54] and our data thermal stability of sulfur on the  $(NH_4)_2S_x$  - treated InP(100) surface is rather high (see, for instance, fig.4 from [54]) and only above  $500^{\circ}C$  sulphur atoms can be completely removed from the surface, heated inside UHV chamber. So, the method of passivation can not be used for temperature-reduced epitaxy important for

OEIC fabrication. The result of passivation is also highly dependent on purity of the ammonium sulfide solution.

# 2.3.2.3. Cleaning procedures

Different procedures were used that to clean InP substrates[10-33]. As a rule, all of them include chemico-mechanical polishing (15 - 60 s in 0.5 - 2 vol % bromine methanol solution), rinsing in running deionized water (RDIW) and drying in pure helium or N<sub>2</sub> gas of the substrate which just after the treatments was transferred into UHV growth chamber. (Some authors, for instance, Couturier et al. [27] before the chemico-mechanical treatment recommended to boil wafers in trichlorethylene and to immerse them for 10 min in a HF(49%)-CH<sub>3</sub>OH solution. Additionally before transferring into UHV system the samples can be degreased ultrasonically in trichlorethane, acetone, methanol and water (Sinharoy et al. [26]) as well as they can be 1-2 min etched at room temperature with H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O (2:1:1) mixture and again rinsed.

In spite of these thoroughly fulfilled procedures the wafers still were contaminated with carbon and oxigen, as observed at AES (our data) or XPS (Weiss et al [29]) analyses, therefore carefully prepared samples must be heated and annealed inside UHV chamber under RHEED, AES or other surface diagnostics. Depending on quality of the pre-treatments outside the chamber the temperature interval of the surface heating and annealing is 350-500°C. Care had be taken to avoid annealing temperatures above 350°C, because at these temperatures the phosphorus desorbs and metallic indium is generated on InP surface. Additional argon ion bombardement using 0.5 or 1.0 KeV ion for various duration (up to 1h) and maintaining the substrate at room temperatures or at temperatures ranging from 250 to 350°C can be used together or without postanneals at temperatures up to 370°C. As a result of the noted above procedures a well-ordered and stoichiometric surface with a negligible amount of surface defects and contaminations was obtained.

However, the described cleaning procedures have serious disadvantages. They are long and complicated and do not garantee a good result due to possible defect initial state of the surface, insufficient purity of chemicals. Heating and annealing of the samples at high temperatures lead to decomposition of InP surface. That to avoid the decomposition it is necessary to have an additional P<sub>2</sub> source supplying phosphorus overpressure over 500°C heated InP(100) surface, that complicates the growth procedure and makes impossible temperature-reduced epitaxy important for OEIC fabrication. But the noted above treatments were actual for early stage of IIa group fluorides growth onto InP substrates (1981-1993).

At present time the Japan Energy Corporation (JEC, formely Nippon Mining and then Nikko Kyodo Co LTD) distributes newly-developed InP wafers for epitaxial growth [55] which give an opportunity to grow crystalline semiconductor or dielectric layers onto InP samples without any pre-treatment, such as cleaning or passivation. It is difficult to render from the paper [55] published according to publicity rules the treatments procedures and the technological regimes developed by JEC for InP wafers. More important is the fact that the new wafers produced by JEC can be used directly for the film growth without any pre-treatment and the result will be better than one obtained with the same wafers but treated anyhow before the film growth. A short rewiev of the paper [55] show the following.

That to use InP substrate directly without any pre-treatment before epitaxial growth JEC has developed new cleaning and packaging technology. In the newly-developed InP wafers technology, substrates polished and cleaned to top quality (strong Kikuchi lines from the InP surface indicate on it) are packaged industrially in nitrogen gas using aluminium laminated packaging sheets. The quality of these wafers has been also examinated by epitaxial single layers and epitaxial heterostructures grown onto InP. It was found that the new substrates have thinner native oxide layer and less silicon contamination compared with the conventional ones as well as that the surface quality can be held for six month with good

mobilities for grown epitaxial layers. It was also shown that InP epitaxial layers grown onto these substrates have 1.5-1.6 times higher electron mobilities, 2-5 times less carrier concentration as well as more intense and distinct exciton luminescence (including the free exciton band) compared to the results obtained with epitaxial layers grown on the same, but conventionally pretreated substrates.

From the systematic studies fulfilled by JEC it was found that its technologies are very effective and provide high quality InP wafers. The reason why JEC's substrates do not need surface pretreatment may be due to cleaning abilities of the Corporation. It is established that cleaning and drying of the surface just after polishing is very important, because the surface quality is mainly determined at these procedures. JEC's clean rooms for polishing and cleaning, chemicals and ultra high water are strictly controlled that to avoid any contamination. Probably, the authors of the paper [55] presenting JEC'c achievements in this field are right that if the surface is contaminated during these processes, the quality can not be recoverd by the customers' side cleaning. Our own experience also confirms this statement. Moreover, it was noticed by us that contaminations from air introduced to JEC's prepared wafers (for instance, due to an illegal custom-house controll with damage of JEC's hermetic packs as it was in our case) can be easily removed by degreasing in pure solvents or under dry vacuum. The deep etching of conventional wafers may recover the surface quality but the surface flatness will have deteriorated.

Concerning the quality of InP epitaxial layer surface it must be noted that it depends on qualities of substrates and epitaxial technology. As a rule the quality of InP epitaxial layers is higher then the quality of conventional InP wafers. InP epitaxial layers, produced by the Rome Laboratory do not need a deep pretreatment and show a good quality of the surface.

Taking into account all the data on InP surface cleaning and passivation, in our experiments we applied deep cleaning and passivation for conventional wafers from IAP ASM, no or very small (if JEC's packaging was deteriorated) pretreatments for newly-developed JEC's wafers as well as weak degreasing and etching for InP epitaxial layers grown at Rome Laboratory.

# 2.3.3. Requirements to dielectrics

Dielectrics selected for epitaxial growth onto semiconductor surfaces must meet the following requirements.

- 1. It is necessary to have strong chemical bonds at the semiconductor-insulator interface, so an insulating material must have similar to semiconductor crystal structure and react with it that the chemical bonds were arranged perpendicular to the interface.
- 2. That to decrease the misfit dislocation density the lattice parameter of the insulator must be close to the lattice parameter of the semiconductor.
- 3. That to avoid strong mechanical tensions during thermal treatment of the grown heterostructure thermal expansion coefficients of semiconductor substrate, dielectric layer and semiconductor layer must be close to each other.
- 4. An other obvious requirement exsistence of a method of epitaxial growth of the chosen insulator onto semiconductor surface. This method must supply high pressure of the insulator constituents at reasonable temperatures. MBE is suitable for this purpose.
- 5. Grown insulator layer must be stable at high temperatures that to meet all the next thermal treatments.
- 6. At last, the grown crystalline dielectric must be a good insulator that usually correlates with broad band gap.

Table.2 shows the basic properties of dielectrics which meet the above noted requirements. The lattice parameters of (CaSrBa) fluorides and some advanced semiconductors are presented in Table.3. One can see that group II-a fluorides are good

materials for all of group III-V materials, in particular, SrF<sub>2</sub> and BaF<sub>2</sub> as well as their combinations can be used for epitaxial growth of crystalline dielectric films onto InP(100). Fuorides on the base of Rare Earth elements (Table 2) are interesting only for epitaxial growth onto (111) surface. The essential advantage of all the fluorides is their high molecular chemical bond energies (Appr. 200 CC/mol) that leads to molecular sublimation of the fluorides and gives an opportunity to prepare their stoichiometric compositions. On the other hand, relatively high thermal expansion coefficients of some fluorides compared to semiconductors lead to definite troubles at thermal treatments of heterostructures.

Table.2. Properties of candidates for insulator/Si and III-V compound epitaxy

| Compound         | Crystal structure | Lattice<br>constant | αx10 <sup>6</sup> K <sup>-1 a</sup><br>(298°K) | ε    | Melting<br>point (°C) | Band<br>gap (eV) |
|------------------|-------------------|---------------------|--|------|-----------------------|------------------|
| KF               | NaCl              | 5.34                | 31   | 5.8  | 858                   | ~11              |
| RbF              | NaCl              | 5.64                | 27   | 6.2  | 795                   | ~10              |
| LiCl             | NaCl              | 5.13                | 44   | 11.3 | 605                   | ~10              |
| LiBr             | NaCl              | 5.49                | 49   | 12.1 | 801                   | ~8               |
| NaCl             | NaCl              | 5.628               | 40   | 5.9  | 550                   | ~8               |
| $.CdF_{2}$       | Cubic fluorite    | 5.3880              | 19   | 8.3  | 1100                  | 8                |
| CaF <sub>2</sub> | Cubic fluorite    | 5.4640              | 19   | 6.8  | 1423                  | 12.1             |
| SrF <sub>2</sub> | Cubic fluorite    | 5,7996              | 18   | 6.5  | 1473                  | 11.25            |
| BaF <sub>2</sub> | Cubic fluorite    | 6.2001              | 18   | 7.4  | 1355                  | 11.0             |
| LaF <sub>3</sub> | Hexagonal         | a=4.148             | 17°  | -    | 1493                  | -                |
| NdF <sub>3</sub> | Hexagonal         | a=4.060             | 1 <b>7°</b>                                    | -    | 1374                  | -                |
| CeF <sub>3</sub> | Hexagonal         | a=4.107             | 13°  | -    | 1430                  | -                |

a.linear thermal expansion coefficient; b.relative permittiviti; c.basal plane thermal mismatch

Table.3. Lattice constants for Ha group fluorides and advanced semiconductors

| NaCl Ty  | No CL Tura |     |                |            |     | 1   |     |     |     | · 1 ·            |          |     |    |
|--|------------|-----|----------------|------------|-----|-----|-----|-----|-----|------------------|----------|-----|----|
|  | Naci Type  |     |                | •          |     |     |     | PbS | PbS | e S              | nTe '    | PbT | 8  |
|  | Hexagonal  |     |                |            |     | · 1 |     |     |     | 1                |          |     |    |
| Semicon-<br>ductor   | ZnS Type   | ZnS | -              | Zn         | Se. | C   | dS. | C   | dSe |                  |          | •   |    |
| Films  | Cubic ZnS  |     | ļ<br>1         | <u>:</u> ] |     | ļ   |     |     |     | i .              |          |     |    |
|  | Туре ·     | Ga  | P              | Ga.        | ВΑ  |     | InP | · I | аÅя |                  |          | InS | ь  |
|  | Dlamond    |     | )<br>)         |            |     | 1   |     |     |     | 1                |          |     |    |
|  | Туре       | SI  |                | G          | e   |     |     |     |     | •                |          | α-: | Sn |
| Fluoride   | 0-5-7      |     |                |            |     |     |     |     |     |                  |          |     |    |
| Films CaF <sub>2</sub> Type                                      |            | Са  | F <sub>2</sub> | •          |     | SrF | 2   | •   | E   | BaF <sub>2</sub> |          |     |    |
| Equivalent Lattice<br>Constant a in Hexa-<br>gonal Structure (Å) |            |     |                |            |     |     |     |     |     |                  | <u>.</u> |     |    |
|  |            | 3.8 |                | . 4        | .0  |     | 4   | .2  |     | 4.4              |          | 4   | .в |
| Lattice Constant a in<br>Cubic Structure (Å)                     |            |     |                |            |     |     |     |     |     |                  |          |     |    |
|  |            | 5.4 |                | 5.6        |     | 5.8 |     | 6,0 | •   | 6.2              | 6.       | 4   |    |

# 2.3.4. Experimental facilities for SS, SCD and SCDS growth

Ultra-high vacuum system for MBE of IIa group fluorides is shown in Fig.6. The main parts of the system are growth chamber, block of effusion (Knudsen) cells and free of oil pumping facilities providing up to 10<sup>-8</sup> Pa of residial atmosphere. Heater of the samples is surrounded by cryoshrouds which improve the work vacuum and protect samples from contaminations. Residual atmosphere and in situ quality of substrate surface, interface and grown fluoride layer are monitored respectively by mass-spectrometer and RHEED systems. Patterns of electron diffraction are registered by high-sensitive television receiver and through special interface introduced into computer's processor. Growth rate and thickness of fluoride layers have been measured with the help of 5 MHz calibrated piezo-electric quartz resonator mounted beside the sample at the growth chamber. Thickness can be measured also with the help of an ellipsometer.

A special diagnostic chamber equipped by AES with argon ion gun and LEED as well as X-ray diffraction have been used for investigation of grown (SrBa)F<sub>2</sub>/InP(100) structures.

The ultra-high vacuum growth chamber equipped MBE and LVE facilities and in situ diagnostics (see Fig.1 of Chapter 2.2) for future growth and investigation of SCDS heterostructures and some OEICs as well as an ellipsometer system with special hard- and software for thin film investigation also have been elaborated.

# 2.3.5. Growth and investigation of (Sr,Ba)F<sub>2</sub>/InP(100) heterostructures

As a result of our investigations on cleaning and passivation procedures of bulk and epitaxial InP a method consisting of etching in  $H_2SO_4$ : $H_2O_2$ : $H_2O$  solution, passivation in  $(NH_4)_2S_x$ , drying and final cleaning of a specimen by heating in ultra-high vacuum chamber have been developed according to the papers [53, 54] (see **2.3.2. InP(100) substrate characterization, cleaning and passivation**). It was shown that a well-ordered and clean surface can be obtained at UHV conditions if samples were heated and annealed above  $500^{\circ}C$  and if an additional  $P_2$  pressure source is introduced into the growth chamber that to surpress In droplets generation and to remove sulfur atoms from the surface. Due to the fact that a good (Sr, Ba) $F_2$  /InP(100) heterostructures can be grown on newly-developed JEC's wafers and epitaxial InP layers at the temperatures considerably less than  $500^{\circ}C$  we did not use the method of passivation in growth experiments.

For preliminary growth experiments we used (BaF<sub>2</sub>)/InP(100) system. As-chemico-mechanically etched 1° off toward [100]InP(100) polished 15x8 mm samples from IAP ASM were appr.5 min degreased in boiling trichlorethilene, rinsed in methanol and RDIW, freshly 1-2 min etched in H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>O (2:1:1) solution, 10 min rinsed again in RDIW, blown dry in pure N<sub>2</sub> gas and then immediately transferred into the growth chamber through a sample load lock. The samples were heated up to 470°C and annealed at this temperature during 10 min at appr. 10<sup>-8</sup> Pa of residual pressure. Substrate cleaning and film growth were monitored in situ by RHEED. Distinct electron reflection spots were seen from clean surface and grown layer. After the substrate exhibited well-ordered and clean surface thin (appr. 0.1µ) BaF<sub>2</sub> layers were grown on these substrates at 350°C and at growth rate of appr. 2 nm/mim from a graphite crucible loaded with bulk crystalline BaF<sub>2</sub> heated up to 1260°C.

The films grown on 1° off toward [100] InP(100) substrates according RHEED and X-ray diffraction data have grains with (100) and (111) orientation. Note that the (100) grains grow parallel to (100) planes of the substrate, but the (111) grains are parallel to physical surface of the substrate and specific part of the (111) grains increases with aftergrowth annealing. The same behaviour is noticed during a course of LRL works in  $CaF_2$  grown on (1-4)° of toward [100]Si(100). The halfwidth W(2 $\Theta$ ) of ( $\Theta$ -2 $\Theta$ ) X-ray diffraction peak from (200) plane of BaF<sub>2</sub> as measured with a single-crystal diffractometer was ) 0.20° compared with 0.10° from (200) plane of InP substrate.

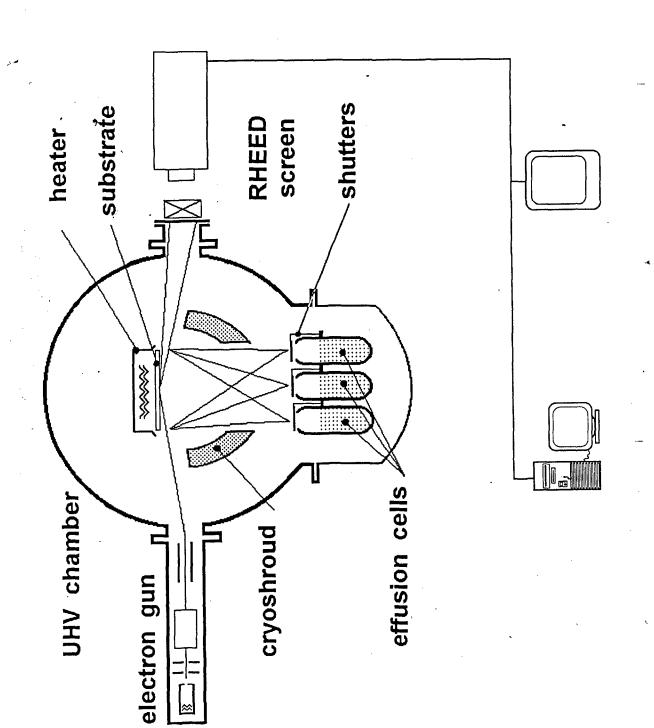


Fig. 6. Experimental set-up for MBE growth of IIa group fluorides on semiconductors

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The next growth experiment was made with epitaxial layer grown on exact (our error in X-ray measurements was appr.  $0.02^{\circ}$ ) oriented InP(100) substrate from Rome Laboratory. In this case that to exclude possible contaminations we used only a weak heating (less than  $500^{\circ}$  C during appr. 10 min) in UHV chamber at  $10^{-8}$  Pa. As a result surface of the substrate had distinct (2x1) structure, O and C contents were less than 0.1 ML, but a few tenth of micron In dpoplets were generated onto the surface if the annealing temperature was appr.  $500^{\circ}$  C, while at the temperatures around  $400^{\circ}$  C we had rather perfect single-crystal film practically without In droplets.  $0.1\mu$  BaF<sub>2</sub> film was grown on that sample at the same above mentioned conditions. W( $2\Theta$ ) peak from the film was equal to  $0.58^{\circ}$  compared with  $0.11^{\circ}$  from epilayer as well as Kikuchi lines on the film surface could be seen by SEM method. The results on ( $\Theta$ - $2\Theta$ ) and ( $\Theta$ - $\Theta$ ) X-ray scan are presented in the table 4.

Table.4.  $W(\Theta)$  and  $W(2\Theta)$  as measured with one-crystal X-ray diffractometer (grad)

| Specimen     | 1° off Chohralsky |             |              | Exact (100) epilayer |             |  |
|--------------|-------------------|-------------|--------------|----------------------|-------------|--|
| Halwidth     | $W(2\Theta)$      | $W(\Theta)$ |              | $W(2\Theta)$         | $W(\Theta)$ |  |
| Reflection   |                   |             |              |                      |             |  |
| $(200)BaF_2$ | 0.20              | 0.86        | $(600)BaF_2$ | 0.58                 | 0.67        |  |
| $(111)BaF_2$ | 0.25              | 0.72        | -            | -                    | -           |  |
| (200)InP     | 0.10              | 0.22        | (600)InP     | 0.11                 | 0.23        |  |
|              |                   |             |              |                      |             |  |

Thus, the results obtained with oblique cutted InP(100) surface show that the dielectric layer morphology is epitaxial with the morphology of clean InP surface as well as that, in spite of big mismatch in the lattice parameters of BaF<sub>2</sub> and InP ( $\sim 5.6\%$ ) single crystal dielectric layers can be obtained on exact oriented InP(100) surface at rather low growth temperature (350° C and less). Only the necessity to clean substrates cutted from conventional InP wafers by heating at ultra-high vacuum leads to additional heating above this growth temperature (it can be a negative factor at OEIC fabrication) as well as to additional introduction into the UHV chamber P<sub>2</sub> source to prevent generation of In droplets.

For final growth experiments pure bulk single-crystal  $SrF_2$  and newly-developed by Japan Energy Corporation InP(100) wafers were used due to the facts that mismatch between lattice parameters is only appr. 1.2% and the fluoride layer can be grown without any pretreatment of substrates. However, some substrates if the packaging of JEC' wafers was deteriorated during custom-house procedures were washed up for a few minutes in boiling pure trychlorethilene, rinsed in RDIW (14  $M\Omega/cm$ ), 1 min etched in  $H_2SO_4:H_2O_2:H_2O$  (2:1:1) for creation af protective P-oxide layer and dryed in pure  $N_2$  gas. Just after extraction from JEC's packaging or the noted above weak pretreatment 8x15 mm substrates were glued with Ga at 50°C in  $N_2$  gas atmosphere to Si satellite and transferred through load lock into UHV growth chamber. RHEED diffraction patterns just after the loading show Kikuchi lines on a strong diffusional background that correlates with the image of InP surface covered with thin protective P-oxide layer (see Fig.7a). Note, that C and O concentrations according to our data on AES were less than 0.1%ML.

After heating and annealing at  $350^{\circ}\text{C}$  the diffusional background was very weak and RHEED patterns show bright Kikuchi lines that corresponds to free of P-oxide InP(100) surface (Fig.7b) . To the moment of end of annealing SrF<sub>2</sub> cell was heated up to  $1260^{\circ}\text{C}$  with closed shutter. Then the shutter was open and  $0.05\mu$  and  $0.4\mu$  dielectric film were grown at  $350^{\circ}\text{C}$  with the rate of 2nm/min. During the growth pressure inside UHV chamber did not exceed of  $10^{-7}$  Pa . After the beginning of SrF<sub>2</sub> layer growth Kikuchi lines step by step were transformed into the net of distinct spots (Fig.7c,d). These patterns of RHEED diffraction testify to creation of SrF<sub>2</sub>(100) surface having (111) microfacets. The most distinct spots were

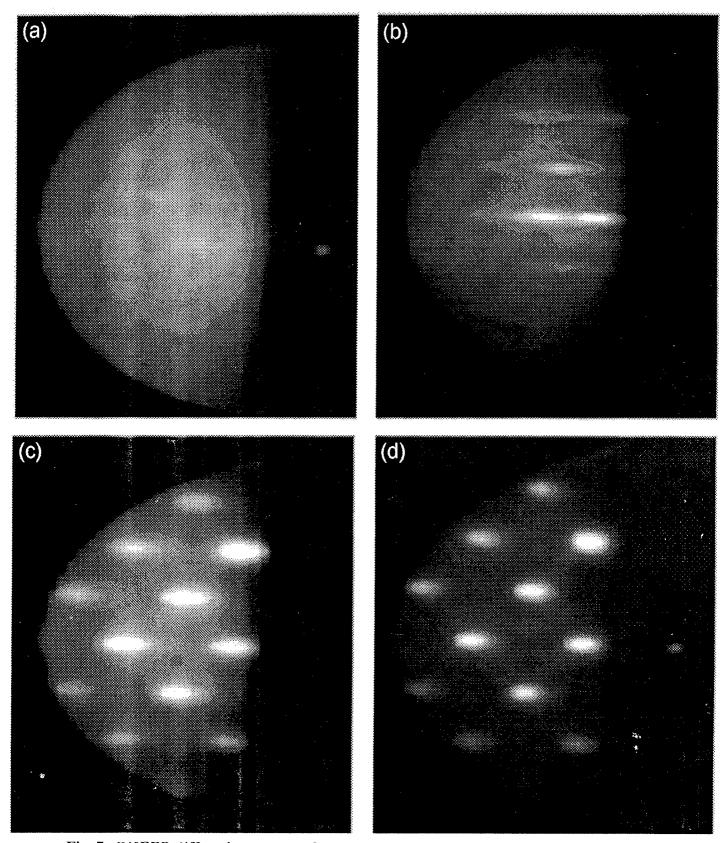


Fig. 7. RHEED diffraction patterns for various stages of SrF2 growth onto InP(100)

- a) as-loaded surface of InP(100)
- b) InP (100) surface after removing of protective P-oxide layer c)  $SrF_2$  surface 1 min after beginning of the growth
- d) the surface of 0.4  $\mu$  thickness SrF<sub>2</sub> layer grown onto InP(100) substrate.

observed in  $0.4~\mu$  SrF<sub>2</sub> films that confirms the results on RBS measuments obtained by Barriere et al [32] which have shown that after  $0.05~\mu$  the films are well crystallized and have the same orientation as the substrate.

# 3. SUMMARY

We report on preparation and characterization of (CaSrBa)F<sub>2</sub>/ InP(100) heterostructures. Taking into account known literature data and experience of the Laser Research Laboratory in epitaxial growth of semiconductor and dielectric films by Laser Vacuum Epitaxy and Molecular Beam Epitaxy methods optimal cleaning and passivation procedures as well as temperature-reduced growing process of BaF<sub>2</sub> / InP(100) (5.65%.mismatch) and SrF<sub>2</sub> / InP(100) (1.18% mismatch) heterostructures were chosen and newly developed. Passivation is necessary that to keep samples in conventional atmospheric conditions and can be used for epitaxial growth at the temperatures above 500°C. Cleaning procedures were effective for MBE epitaxial growth of 0.1 µ BaF<sub>2</sub> films in UHV chamber at 350°C onto conventional polished 1° off toward [100] InP(100) wafers as well as onto epitaxial InP(100) substrates. Epitaxial growth means texturized film with (100) and (111) grains parallel to (100) plane and physical surface of the substrate respectively in the case of oblique cutted wafers and and single crystal film in the case of exact (100)-oriented epitaxial substrate. 0.05µ and 0.4µ SrF<sub>2</sub> single-crystal films were MBE grown in UHV chamber at 350°C without or with very simple temperature-reduced pretreatment onto substrates from specially prepared and individually packed InP(100) wafers produced by Japan Energy Corporation. Experimental facilities of the Laser Research Laboratory were improved in the course of present work that to be able to grow by MBE and/or LVE in common cycle semiconductor-semiconductor (SS) and semiconductor-crystalline dielectric-semiconductor (SCDS) heterostructures for OEIC.

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